Chem. Mater. **2007,** *19,* 6195–6205

Syntheses and Electropolymerization of Carboranyl-Functionalized Pyrroles and Thiophenes

Erhong Hao,[†] Bruno Fabre,[*,‡] Frank R. Fronczek,[†] and M. Graça H. Vicente[*,†]

Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803, and Matière Condensée et Systèmes Electroactifs MaCSE, Sciences Chimiques de Rennes, Unité Mixte de Recherche No. 6226 CNRS/Université de Rennes 1, Campus de Beaulieu, 35042 Rennes Cedex, France

Received July 19, 2007. Revised Manuscript Received September 28, 2007

A series of 3- and 3,4-substituted pyrroles and thiophenes with electron-withdrawing carboranylmethylphenyl groups has been synthesized in high yields via the coupling of either pyrrole- and thiopheneboronic acids with carboranylmethylphenyl halides or bromo-functionalized pyrroles with carboranylmethylphenylboronic acid. Some of these compounds were efficiently electropolymerized in acetonitrile or dichloromethane. The resulting conducting polymer films were reversibly p-doped in the range 0.0–0.25 V vs Ag/Ag$^+$ 10^{-2} M for the pyrrole-based polymers and p-/n-doped at ca. 0.60 and −1.90 V for the thiophene-based polymers. As a consequence of the presence of the carborane cages, the electroactivity of the polythiophenes was not degraded when highly oxidizing potentials (up to 2.0 V) were applied. In contrast, the polypyrrole derivatives were rendered totally electroinactive under similar conditions. The UV–vis spectroscopy analysis of the electrogenerated polymers revealed that the introduction of carborane cages resulted in either an enhancement or a stabilization of the mean conjugation length of the resulting polymers in comparison with the reference phenyl-substituted polypyrrole and polythiophene. In addition, these functionalized materials show unusual thermal stability for conducting polymers with a mass loss less than 10% up to 500 °C, under an inert atmosphere.

1. Introduction

Heterocyclic conjugated polymers, such as polypyrrole and polythiophene, have important applications as conducting electroactive materials, in electrochemical switching, energy storage and conversion, photovoltaics, electrochromic windows, electromechanical devices, and in chemical and physical sensing.[1–4] The electrochemical polymerization of pyrrole and thiophene monomers is a fast and reliable method for the generation of functional polymers onto a conducting surface, with a desired thickness. Both macro- and microelectrodes of different shapes and with thicknesses ranging from nanometers to micrometers have been used for the electrodeposition of uniform films.[5–8] The conductivity properties of the electrogenerated polymers obviously depends on the structure of the monomers used and on their stability under the polymerization conditions. In particular, it has been observed that the functionalization of pyrrole and thiophene monomers at the 3- and/or 4-positions with electron-withdrawing group(s) linked via conjugated bridges significantly decreases the polymerization potential and consequently the overoxidation of the forming polymer, while increasing the photovoltaic polymer performance.[9] The functionalization of conjugated polymers with organoborane groups is particularly attractive because of their electron-deficient nature.[10] For example, it was recently reported that the introduction of dimesitylboryl groups at the periphery of thiophenes significantly decreases the LUMO energy levels of the resulting polymers, as it was evidenced by strong bathochromic shifts in the absorption and emission spectra as well as by the observation of reversible reduction waves occurring at significantly less cathodic potentials.[11] Our group has been interested in the preparation of conducting electroactive polypyrroles from carboranyl-substituted pyrroles.[12–14] Carboranes, in both neutral and anionic forms, are boron clusters with delocalized electrons and unique properties including high hydrophobic character and remarkable high chemical stability. Several carborane-containing organic

---

[*] Corresponding authors. E-mail: vicente@lsu.edu; bruno.fabre@univ-rennes1.fr.

[†] Louisiana State University.

[‡] Unité Mixte de Recherche No. 6226 CNRS/Université de Rennes 1.

(1) Lu, W.; Fadeev, A. G.; Qi, B.; Smela, E.; Mattes, B. R.; Ding, J.; Spinks, G. M.; Mazurkiewicz, J.; Zhou, D.; Wallace, G. G.; MacFarlane, D. R.; Forsyth, S. A.; Forsyth, M. *Science* **2002**, *297*, 983.

(2) Yu, H. H.; Pullen, A. E.; Buschel, M. G.; Swager, T. M. *Angew. Chem., Int. Ed.* **2004**, *43*, 3700.

(3) Bashyam, R.; Zelenay, P. *Nature (London)* **2006**, *443*, 63.

(4) Grenier, C. R. G.; Pisula, W.; Joncheray, T. J.; Mullen, K.; Reynolds, J. R. *Angew. Chem., Int. Ed.* **2007**, *46*, 714.

(5) Holdcroft, S. *Adv. Mater.* **2001**, *13*, 1753.

(6) LaVan, D. A.; George, P. M.; Langer, R. *Angew. Chem., Int. Ed.* **2003**, *42*, 262.

(7) Carswell, A. D. W.; O'Rear, E. A.; Grady, B. P. *J. Am. Chem. Soc.* **2003**, *125*, 14793.

(8) Chen, A.; Wang, H.; Li, X. *Chem. Commun.* **2005**, 1863.

(9) (a) Cutler, C. A.; Burrell, A. K.; Officer, D. L.; Too, C. O.; Wallace, G. G. *Synth. Met.* **2001**, *123*, 225. (b) Cutler, C. A.; Burrell, A. K.; Collis, G. E.; Dastoor, P. C.; Officer, D. L.; Too, C. O.; Wallace, G. G. *Synth. Met.* **2001**, *123*, 35.

(10) Zhao, C.-H.; Wakamiya, A.; Inukai, Y.; Yamagucgi, S. *J. Am. Chem. Soc.* **2006**, *128*, 15934.

(11) Li, H.; Sundararaman, A.; Venkatasubbaiah, K.; Jäkle, F. *J. Am. Chem. Soc.* **2007**, *129*, 5792.

(12) Fabre, B.; Chayer, A.; Vicente, M. G. H. *Electrochem. Commun.* **2003**, *5*, 431.

(13) Fabre, B.; Clark, J. C.; Vicente, M. G. H. *Macromolecules* **2006**, *39*, 112.

(14) Clark, J. C.; Fabre, B.; Fronczek, F. R.; Vicente, M. G. H. *J. Porphyrins Phthalocyanines* **2005**, *9*, 803.

10.1021/cm701935n CCC: $37.00

molecules have been synthesized in the past decades, and some of these are currently finding applications in medicine[15,16] and in material science.[17–19] It has been generally observed that the presence of carborane group(s) increases the thermal and chemical stability of the host molecules and enhances their photo- and electrochemical properties. Several polymers containing carborane groups, usually linked to the host molecule by aromatic spacers, have been synthesized and characterized.[12–14,20–26] In general, these materials show high resistance to oxidation and remarkable thermal and photochemical stabilities. Furthermore, the presence of carborane groups within an electronically conducting polymer film, either as immobilized doping anions or covalently bonded, has been shown to reduce the communication between the electrolyte anions and the polymer backbone due to their large size and high hydrophobicity. In addition, the electron-deficient nature of carborane groups could significantly reduce the energy of the π–π* transitions. We[12,13] and others[24,25] have recently reported that redox-active polypyrroles containing covalently linked carborane groups exhibit higher electrochemical stability and overoxidation resistance compared to unsubstituted polypyrrole. Herein we report the synthesis and electropolymerization of a new series of 3- and 3,4-substituted pyrroles and thiophenes with neutral and anionic carborane groups, linked by phenylmethyl bridges. Our general methodology to these types of molecules involves palladium-catalyzed cross-coupling reactions between readily available pyrrole and thiophene boronic acids and carboranylaryl halides. The polymerization conditions and electrochemical characterization of the polymers generated from this series of compounds are compared and discussed. It is known that thiophene monomers undergo electropolymerization via radical cation intermediates rather than radical anions as in the case of pyrrole monomers. Since radical cations are normally generated at higher oxidation potentials, the electrochemical polymerization of thiophenes is a more challenging process due to overoxidation.[27–29] Also of interest, their electrochemical resistance to oxidizing potentials is examined as a function of the nature of the polymer matrix and the number of linked carborane cages per monomer unit. Finally, the UV–vis spectroscopy and TGA characterizations of the functionalized polymers are also reported in order to obtain further insights into their electronic properties and their thermal stability.

2. Experimental Section

2.1. Synthesis. All reactions were monitored by TLC using 0.25 mm silica gel plates with or without UV indicator (60F-254). Carborane was detected by emerging into $PdCl_2$ in aqueous HCl solution (1 g $PdCl_2$ in 80 mL of water and 20 mL of concentrated HCl solution) and heated to see black spot on TLC. Silica gel (Sorbent Technologies, 32–63 μm) was used for flash column chromatography. ^{1}H and ^{13}C NMR were obtained on either a DPX-250 or an ARX-300 Bruker spectrometer. Chemical shifts (δ) are given in ppm relative to $CDCl_3$ (7.26 ppm, ^{1}H) or CD_2Cl_2 (5.32 ppm, ^{1}H) unless otherwise indicated. Electronic absorption spectra were measured on a Perkin-Elmer Lambda 35 UV–vis spectrophotometer. MALDI-TOF mass spectra were obtained on an Applied Biosystems QSTAR XL, using the positive method with dithranol as matrix unless otherwise indicated. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Compounds **12**[43] and **17**[44] were prepared according to the literature.

2.1.1. Carboranylboronic Ester 2. A solution of 1-methyl-*o*-carborane (530 mg, 3.35 mmol) in dry THF (15 mL) in a 100 mL Schlenk tube equipped with a magnetic stirrer was cooled to 0 °C with an ice bath. A solution of *n*-butyllithium (3.69 mmol, 2.5 M solution in hexane) was added dropwise at 0 °C. The final mixture was warmed to room temperature and stirred for 1 h before being cooled to −78 °C. A solution of compound **1** (1.00 g, 3.35 mmol) in dry THF (5 mL) was added dropwise to the reaction mixture at −78 °C. The final mixture was warmed to room temperature and stirred overnight until complete disappearance of the starting materials by TLC analysis. The mixture was poured into 50 mL of brine and extracted with ethyl acetate (3 × 50 mL) and dried over anhydrous Na_2SO_4, and the resulting residue was purified by column chromatography on silica gel, using CH_2Cl_2/hexane 1:1 for elution. The title compound was obtained as a white powder (1.15 g) in 91% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.85 (2H, d, $J = 7.76$ Hz), 7.23 (2H, d, $J = 7.81$ Hz), 3.49 (2H, s), 2.19 (3H, s), 1.5–3.5 (10H, br), 1.41 (12H, s). ^{13}C NMR (75 MHz, $CDCl_3$): δ 139.5, 136.6, 131.3, 85.6, 79.0, 78.3, 42.9, 26.5, 25.3. HRMS (ESI) $[M - C_2H(CH_3)_4]^-$: 291.2535, calcd for $C_{10}H_{20}B_{11}O_2$: 291.2565.

2.1.2. Carboranylboronic Acid 3. To a mixture of boronic ester **2** (187 mg, 0.50 mmol), $NaIO_4$ (321 mg, 1.5 mmol) and ammonium acetate (116 mg, 1.5 mmol) were added 15 mL of acetone and 5 mL of water. The reaction mixture was stirred overnight at room temperature and under air until complete disappearance of boronic ester **2** by TLC analysis. The mixture was poured into 25 mL of water and extracted with ethyl acetate (3 × 30 mL). The organic layers were dried over anhydrous Na_2SO_4, concentrated under vacuum, and washed with hexane. The resulting residue was dried under vacuum to yield the title compound as a white powder (130.1 mg) in 89% yield. ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.06 (2H, s), 7.74 (2H, d, $J = 7.75$ Hz), 7.21 (2H, d, $J = 7.86$ Hz), 3.32 (2H, s), 2.21 (3H, s), 1.5–3.5 (10H, br). ^{13}C NMR (75 MHz, DMSO-d_6): δ 137.2, 134.1, 129.5, 78.9, 76.4, 75.2, 40.5, 22.9. HRMS (ESI) $[M - H]^-$: 291.2566, calcd for $C_{10}H_{20}B_{11}O_2$: 291.2565.

2.1.3. Dicarboranylpyrrole 5. 1-(Triisopropylsilyl)-3,4-dibromopyrrole **4** (460 mg, 1.24 mmol), boronic ester **2** (1.15 g, 3.02 mmol), and tetrakis(triphenylphosphine)palladium (138 mg, 0.12

---

(15) Soloway, A. H.; Tjarks, W.; Barnum, B. A.; Rong, F.-G.; Barth, R. F.; Codogni, I. M.; Wilson, J. G. *Chem. Rev.* **1998**, *98*, 1515.
(16) Barth, R. F.; Coderre, J. A.; Vicente, M. G. H.; Blue, T. E. *Clin. Cancer Res.* **2005**, *11*, 3987.
(17) Christopher, A. R. *Acc. Chem. Res.* **1998**, *31*, 133.
(18) Kaszynski, P.; Douglass, A. G. *J. Organomet. Chem.* **1999**, *581*, 28.
(19) Kottas, G. S.; Clarke, L. I.; Horinek, D.; Michl, J. *Chem. Rev.* **2005**, *105*, 1281.
(20) Kabachii, Y. A.; Valetskii, P. M. *Int. J. Polym. Mater.* **1990**, *14*, 9.
(21) Schöberl, U.; Magnera, T. F.; Harrison, R. M.; Fleischer, F.; Pflug, J. L.; Schwab, P. F. H.; Meng, X.; Lipiak, D.; Noll, B. C.; Allured, V. S.; Rudalevige, T.; Lee, S.; Michl, J. *J. Am. Chem. Soc.* **1997**, *119*, 3907.
(22) Colquhoun, H. M.; Herbertson, P. L.; Wade, K.; Baxter, I.; Williams, D. J. *Macromolecules* **1998**, *31*, 1694.
(23) Fox, M. A.; Wade, K. *J. Mater. Chem.* **2002**, *12*, 1301.
(24) (a) Masalles, C.; Borros, S.; Vina, C.; Teixidor, F. *Adv. Mater.* **2000**, *12*, 1199. (b) Masalles, C.; Borros, S.; Vina, C.; Teixidor, F. *Adv. Mater.* **2002**, *14*, 449.
(25) Masalles, C.; Llop, J.; Vina, C.; Teixidor, F. *Adv. Mater.* **2002**, *14*, 826.
(26) Kimura, H.; Okita, K.; Ichitani, M.; Sugimoto, T.; Kuroki, S.; Ando, I. *Chem. Mater.* **2003**, *15*, 355.
(27) Krische, B.; Zagorska, M. *Synth. Met.* **1989**, *28*, 263.
(28) Beck, F.; Barsch, U.; Michaelis, R. *J. Electroanal. Chem.* **1993**, *351*, 169.
(29) Wallace, G. G., Spinks, G. M., Kane-Maguire, I. A. P., Teasdale, P. R., Eds.; *Conductive Electroactive Polymers*, 2nd ed.; CRC Press LLC: Boca Raton, FL, 2003.

mmol) were added to a 250 mL Schlenk tube. The reaction tube was vacuumed and refilled with argon three times. Then toluene (20 mL), methanol (4 mL), and 1 mL of 2 M $NaHCO_3$ solution were added via syringe at −78 °C. The reaction mixture was "pumped free throw" three times to remove air and stirred at 70 °C under argon for 2 days. The mixture was cooled to room temperature and poured into 100 mL of brine and extracted with ethyl acetate (3 × 100 mL). The organic layers were dried over anhydrous Na_2SO_4 and concentrated under vacuum. The resulting residue was dissolved in 20 mL of THF, and 1.25 mL of Bu_4NF solution (1.0 M in THF) was added at 0 °C. The reaction mixture was stirred 0 °C for 20 min before being poured into 100 mL of water and extracted with ethyl acetate (3 × 100 mL). The organic layers were dried over anhydrous Na_2SO_4 and concentrated under vacuum. The residue was purified by column chromatography on silica gel, using ethyl acetate/hexane 1:4 for elution. The title pyrrole was obtained as a white powder (222 mg) in 32% yield. ^1H NMR (300 MHz, $CDCl_3$): δ 8.28 (1H, br), 7.18–7.21 (4H, m), 7.05–7.08 (4H, m), 6.94 (2H, d, $J = 2.69$ Hz), 3.45 (4H, s), 2.16 (6H, s), 1.5–3.5 (20H, br). MALDI-TOF $[M + H]^+$: 560.74, calcd for $C_{24}H_{42}B_{20}N$: 560.82. HRMS (ESI) $[M - H]^-$: 558.5032, calcd for $C_{24}H_{40}B_{20}N$: 558.5167.

2.1.4. N-*Triisopropylsilylcarboranylpyrrole 7.* 1-(Triisopropylsilyl)pyrrole-3-boronic acid **9** (147 mg, 0.55 mmol), iodide **10** (188 mg, 0.50 mmol), and tetrakis(triphenylphosphine)palladium (58 mg, 0.05 mmol) were added to a 50 mL Schlenk tube. The reaction tube was vacuumed and refilled with argon three times. Toluene (10 mL), methanol (2 mL), and 0.5 mL of 2 M Na_2CO_3 solution were added via syringe at −78 °C. The reaction mixture was then "pumped free throw" three times to remove air and then stirred at 80 °C under argon for 20 h until complete disappearance of iodide **10** by TLC analysis. The mixture was cooled to room temperature, poured into 50 mL of brine, and extracted with ethyl acetate (3 × 50 mL). The organic layers were dried over anhydrous Na_2SO_4 and concentrated under vacuum. The residue was purified by column chromatography on alumina grade III, using 15% ethyl acetate in hexane for elution. The title pyrrole was obtained as a white powder (209 mg) in 89% yield. ^1H NMR (300 MHz, $CDCl_3$): δ 7.50 (2H, d, $J = 8.19$ Hz), 7.13 (2H, d, $J = 8.31$ Hz), 7.10 (1H, m), 6.82 (1H, m), 6.61 (1H, m), 3.45 (2H, s), 2.16 (3H, s), 1.5–3.5 (10H, br), 1.41 (3H, s), 1.11 (18H, m). MALDI-TOF $[M + H]^+$: 470.745, calcd for $C_{23}H_{44}B_{10}NSi$: 470.782. HRMS (ESI) $[M + Na]^+$: 492.4086, calcd for $C_{23}H_{43}B_{10}NSiNa$: 492.4078.

2.1.5. Monocarboranylpyrrole 8. Pyrrole **7** (47 mg, 0.10 mmol) was dissolved in 5 mL of THF, and this solution was cooled to 0 °C with an ice bath. Then, 0.10 mL of Bu_4NF solution (1.0 M in THF) was added at 0 °C, and the reaction mixture was stirred at 0 °C for 15 min. The mixture was poured into 25 mL of water and extracted with ethyl acetate (3 × 25 mL). The organic layers were dried over anhydrous Na_2SO_4 and concentrated under vacuum. The residue was purified by silica gel column chromatography using ethyl acetate/hexane 1:5 for elution. The title compound was obtained as a white powder (29.8 mg) in 95% yield. ^1H NMR (250 MHz, CD_2Cl_2): δ 8.43 (1H, br), 7.53 (2H, d, $J = 8.19$ Hz), 7.15 (2H, d, $J = 8.31$ Hz), 7.14 (1H, m), 6.84 (1H, m), 6.53 (1H, m), 3.48 (2H, s), 2.18 (3H, s), 1.5–3.5 (10H, br). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 136.1, 132.5, 131.0, 125.4, 124.4, 119.4, 115.2, 106.6, 78.8, 75.7, 41.2, 23.9. MALDI-TOF $[M + H]^+$: 314.367, calcd for $C_{14}H_{24}B_{10}N$: 314.442. HRMS (ESI) $[M - H]^-$: 312.2721, calcd for $C_{14}H_{22}B_{10}N$: 312.2721.

2.1.6. 4-(Carboranylmethyl)phenyl Iodide 10. 1-Methyl-*o*-carborane (325 mg, 2.05 mmol) was dissolved in dry THF (15 mL) in a 100 mL Schlenk reaction tube equipped with magnetic stirring and cooled to 0 °C with an ice bath. 1.00 mL of *n*-butyllithium solution (2.50 mmol, 2.5 M solution in hexane) was added dropwise at 0 °C, and the final mixture was warmed to room temperature and stirred for 1 h. The reaction solution was cooled to −78 °C, and 4-bromomethyliodobenzene (606 mg, 2.05 mmol) dissolved in 5 mL of dry THF was added dropwise. The final reaction mixture was warmed to room temperature and stirred overnight until complete disappearance of the starting materials by TLC analysis. The mixture was poured into 50 mL of brine and extracted with ethyl acetate (3 × 50 mL). The organic layers were dried over anhydrous Na_2SO_4 and concentrated under vacuum, and the resulting residue was purified by column chromatography on silica gel, using 15% ethyl acetate in hexane for elution. The title pyrrole was obtained as a white powder (606 mg) in 79% yield. ^1H NMR (250 MHz, $CDCl_3$): δ 7.67 (2H, d, $J = 8.09$ Hz), 6.92 (2H, d, $J = 8.07$ Hz), 3.39 (2H, s), 2.15 (3H, s), 1.5–3.5 (10H, br). ^{13}C NMR (75 MHz, $CDCl_3$): δ 138.2, 134.9, 132.6, 94.3, 76.8, 74.8, 41.1, 24.1. HRMS (ESI) $[M - H]^-$: 373.1487, calcd for $C_{10}H_8B_{10}I$: 373.1462.

2.1.7. Dicarboranylpyrrole 11. 1-(Triisopropylsilyl)pyrrole-3-boronic acid **9** (547 mg, 2.05 mmol), dicarboranylbromobenzene **12** (996 mg, 2.00 mmol), and tetrakis(triphenylphosphine)palladium (116 mg, 0.10 mmol) were added to a 250 mL Schlenk tube. The reaction tube was vacuumed and refilled with argon three times. Toluene (40 mL), methanol (8 mL), and 4 mL of 2 M Na_2CO_3 solution were added via syringe at −78 °C, and the final mixture was "pumped free throw" three times to remove air. The reaction mixture was stirred at 80 °C under argon for 20 h until complete disappearance of compound **12** by TLC. The mixture was cooled to room temperature, poured into 150 mL of brine, and extracted with ethyl acetate (3 × 150 mL). The organic layers were dried over anhydrous Na_2SO_4 and concentrated under vacuum, and the resulting residue was purified by column chromatography on silica gel, using 15% ethyl acetate in hexane for elution. The *N*-triisopropylsilylpyrrole was obtained as a white powder (1.11 g) in 87% yield. ^1H NMR (300 MHz, $CDCl_3$): δ 7.26 (2H, s), 7.03 (1H, m), 6.83 (1H, s), 6.78 (1H, m), 6.58 (1H, m), 3.47 (4H, s), 2.19 (6H, s), 1.5–3.5 (20H, br), 1.46 (3H, s), 1.13 (18H, m). MALDI-TOF $[M + H]^+$: 641.21, calcd for $C_{27}H_{58}B_{20}NSi$: 641.05. A solution of the N-protected pyrrole (640 mg, 1.00 mmol) in 25 mL of THF was cooled to 0 °C. 1.1 mL of Bu_4NF solution (1.0 M in THF) was added dropwise, and the final mixture was stirred at 0 °C for 15 min. The reaction mixture was poured into 25 mL of water and extracted with ethyl acetate (3 × 100 mL); the organic layers were dried over Na_2SO_4 and concentrated under vacuum. The resulting residue was purified by column chromatography on silica gel, using CH_2Cl_2 for elution. The title pyrrole was obtained as a white powder (465 mg) in 96% yield. ^1H NMR (300 MHz, DMSO-d_6): δ 11.00 (1H, s), 7.37 (2H, s), 7.23 (1H, m), 6.90 (1H, s), 6.81 (1H, m), 6.43 (1H, m), 3.61 (4H, s), 2.25 (6H, s), 1.5–3.5 (20H, br). MALDI-TOF $[M + H]^+$: 484.57, calcd for $C_{18}H_{38}B_{20}N$: 484.72. HRMS (ESI) $[M - H]^-$: 482.4882 calcd for $C_{18}H_{36}B_{10}N$: 482.4854.

2.1.8. Carboranylthiophene 14. 3-Boronic acid thiophene **13** (274 mg, 2.15 mmol), bromobenzene **10** (655 mg, 2.00 mmol), and tetrakis(triphenylphosphine)palladium (116 mg, 0.10 mmol) were added in a 250 mL Schlenk tube. The reaction tube was vacuumed and refilled with argon three times. Toluene (40 mL), methanol (8 mL), and 4 mL of 2 M Na_2CO_3 solution were added via syringe at −78 °C, and the final mixture was "pumped free throw" three times to remove air, before being stirred at 80 °C under argon for 24 h, until complete disappearance of **10** (R = Br) by TLC. The mixture was cooled to room temperature, poured into 150 mL of brine, and extracted with ethyl acetate (3 × 100 mL). The organic layers were dried over Na_2SO_4 and concentrated under

Table 1. Crystal Data, Data Collection, and Refinement Parameters for Compounds 3, 10 (R = I), and 14

compound	**3**	**10**	**14**
CCDC deposit no.	CCDC 649989	CCDC 649990	CCDC 649991
formula	$C_{10}H_{21}B_{11}O_2 \cdot C_2H_6OS$	$C_{10}H_{19}B_{10}I$	$C_{14}H_{22}B_{10}S$
color/shape	colorless plate	colorless lath	colorless lath
formula weight	370.31	374.25	330.48
crystal system	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
temp, K	90	115	90
cell constants			
a, Å	19.767(2)	17.049(3)	18.803(3)
b, Å	7.6608(10)	7.9948(11)	7.8137(12)
c, Å	14.602(2)	12.027(2)	12.159(2)
β, deg	111.660(6)	103.844(7)	101.279(7)
cell volume, Å^3	2055.1(4)	1591.7(4)	1751.9(5)
formula units/unit cell	4	4	4
D_{calc}, g cm^{-3}	1.197	1.562	1.253
μ_{calc}, cm^{-1}	1.67	19.91	1.76
diffractometer/scan	Nonius KappaCCD/ω	Nonius KappaCCD/ω	Nonius KappaCCD/ω
radiation, graphite monochr	Mo Kα ($\lambda = 0.71073$ Å)	Mo Kα	Mo Kα
crystal dimensions, mm	$0.03 \times 0.27 \times 0.35$	$0.08 \times 0.25 \times 0.32$	$0.07 \times 0.15 \times 0.40$
min, max transmission	0.944, 0.995	0.568, 0.857	0.933, 0.988
reflections measured	33530	19894	19953
R_{int}	0.038	0.016	0.025
independent reflections	5295	4454	5425
2θ range, deg	$5.0 < 2\theta < 57.4$	$5.0 < 2\theta < 61.0$	$5 < 2\theta < 61.6$
range of h,k,l	$\pm 26, \pm 10, \pm 19$	$\pm 23, \pm 10, \pm 16$	$\pm 27, \pm 10, \pm 17$
reflctns observed, $I > 2\sigma(I)$	3856	4120	4272
data/parameters	5295/254	4454/192	5425/236
R (obs)	0.044	0.025	0.046
R (all data)	0.071	0.028	0.064
R_w, F^2 (all data)	0.115	0.061	0.119
H atom treatment	constr, OH refined	constrained	constrained
GOF	1.034	1.037	1.022
max resid peaks (e Å^{-3})	0.31, −0.34	0.60, −1.04	0.42, −0.27

vacuum. The resulting residue was purified by column chromatography on silica gel, using ethyl acetate/hexane 1:9 for elution. The title thiophene was obtained as a white powder (620 mg) in 94% yield. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.60 (2H, d, $J = 7.69$ Hz), 7.52–7.53 (1H, m), 7.43–7.44 (2H, m), 7.24 (2H, d, $J = 7.91$ Hz), 3.51 (2H, s), 2.19 (3H, s), 1.5–3.5 (10H, br). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 141.8, 135.8, 134.4, 131.2, 126.8, 126.8, 126.7, 125.5, 121.0, 78.3, 75.7, 41.1, 23.9. MALDI-TOF $[M + H]^+$: 331.65, calcd for $C_{14}H_{23}B_{10}S$: 331.50.

2.1.9. Dicarboranylthiophene 15. 3-Boronic acid thiophene **13** (140 mg, 1.10 mmol), bromobenzene **12** (497 mg, 1.00 mmol), and tetrakis(triphenylphosphine)palladium (58 mg, 0.05 mmol) were added into a 250 mL Schlenk tube. The reaction tube was vacuumed and refilled with argon three times before toluene (20 mL), methanol (4 mL), and 2 mL of 2 M Na_2CO_3 solution were added via syringe at −78 °C. The reaction mixture was "pumped free throw" three times to remove air and stirred at 80 °C under argon for 24 h until complete disappearance of **12** by TLC. The mixture was cooled to room temperature, poured into 100 mL of brine, and extracted with ethyl acetate (3 × 100 mL), and the organic layers were dried over anhydrous Na_2SO_4 and concentrated under vacuum. The resulting residue was purified by column chromatography on silica gel, using ethyl acetate/hexane 1:9 for elution. The title thiophene was obtained as a white powder (461 mg) in 92% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.42–7.47 (1H, m), 7.35–7.37 (2H, m), 7.24 (2H, s), 6.92(1H, m), 3.50 (4H, s), 2.18 (6H, s), 1.5–3.5 (20H, br). MALDI-TOF $[M + H]^+$: 501.89, calcd for $C_{18}H_{37}B_{20}S$: 501.77.

2.1.9. Nido-*carboranylthiophene 16.* To a solution of thiophene **14** (331 mg, 1.00 mmol) in 50 mL of THF was added 2.1 mL of a *n*-Bu_4NF solution (1.0 M in THF). The final mixture was stirred at 60 °C for 2 h, then poured into 50 mL of water, and extracted with ethyl acetate (3 × 50 mL). The organic layers were dried over anhydrous Na_2SO_4 and concentrated under vacuum. The resulting residue was purified by column chromatography on silica gel using ethyl acetate for elution. The title thiophene was obtained as a white powder (505 mg) in 90% yield. ^{1}H NMR (300 MHz, acetone-d_6): δ 7.66–7.67 (1H, m), 7.57–7.60 (2H, m), 7.51–7.53 (2H, m), 7.36–7.39 (2H, m), 3.30–3.39 (8H, m), 3.27 (2H, s), 2.11 (3H, s), 1.76–1.81 (8H, m), 1.5–3.5 (9H, br), 1.40–1.44 (8H, m), 0.91–0.98 (t, 12H), −2.35 (1H, br s, B–H–B). MALDI-TOF $[M - NBu_4]^+$: 320.87, calcd for $C_{14}H_{22}B_9S$: 320.69.

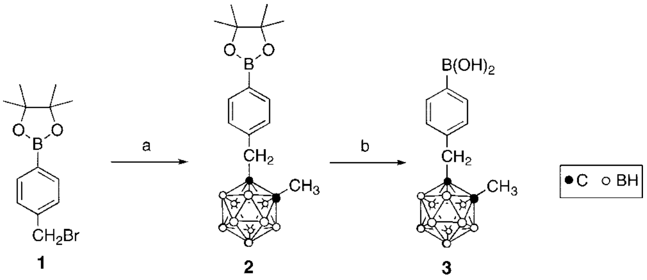
2.2. X-ray Data Collection and Structure Determination. Intensity data were collected at low temperature for compounds **3**, **10**, and **14**, using graphite monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å) on a Nonius KappaCCD diffractometer fitted with an Oxford Cryostream cooler. Data reduction included absorption corrections by the multiscan method. Crystal data and experimental details are given in Table 1. Structures were solved by direct methods and refined by full-matrix least-squares based on F^2, using SHELXL97.[30] C–H hydrogen atoms were treated as riding in idealized positions, and O−H hydrogen atoms for compound **3** were refined. Compound **14** has disorder in its thiophene rings, involving a 2-fold rotation about the bond connecting the phenyl and thiophene rings. Thus, S and C swap positions with approximately 1:1 occupation (refined values 0.519(2):0.481(2)). All residual electron density peaks greater than 1 e Å^{-3} in **10** were located near the iodine position.

2.3. Electrochemical Characterization. Tetra-*n*-butylammonium hexafluorophosphate (Bu_4NPF_6) was purchased from Fluka (puriss, electrochemical grade). Acetonitrile (Merck) was freshly distilled over calcium hydride prior to use. The electrolytic medium was dried in situ over activated, neutral alumina from Aldrich. Alumina was previously activated at 450 °C under vacuum for several hours.

---

(30) Sheldrick, G. M. SHELXL97: Program for the Refinement of Crystal Structures; University of Göttingen: Göttingen, Germany, 1997.

Scheme 1. Reaction conditions: (a) 1-methyl-*o*-carborane, ^{n}BuLi, THF (91%); (b) $NaIO_4$, NH_4OAc, acetone/water, rt (89%)



Linear potential sweep cyclic voltammetry experiments were performed with an Autolab PGSTAT 20 potentiostat from Eco Chemie B.V., equipped with General Purpose Electrochemical System (GPES) software (version 4.5 for Windows). The working electrode was a 1 mm diameter platinum disk (area: 0.8 mm^2), and the counter electrode was a glassy carbon rod. Potentials were relative to the system 10^{-2} M $Ag^+|Ag$ in acetonitrile (+0.29 V vs aqueous SCE). Solution resistance was compensated by positive feedback. All electrochemical measurements were carried out at room temperature (20 ± 2 °C) and under a constant flow of argon.

2.4. UV–vis Spectroelectrochemistry. UV–vis absorption spectra were recorded on a Shimadzu Multispec-1501 spectrophotometer (190–1100 nm scan range) interfaced with a microcomputer for data acquisition, and quartz Suprasil cells from Hellma (1 cm path length) were used. The polymer films were grown on an indium tin oxide (ITO)-coated glass slide electrode.

2.5. TGA. TGA measurements were performed under a nitrogen atmosphere with a Setaram TGA/TDA/DSC balance using a platinum container and a temperature ramp of 10 °C min^{-1}.

3. Results and Discussion

3.1. Synthesis of Carboranylboronic Acid 3. The cross-coupling of organometallic reagents with organic halides and related electrophiles is an efficient methodology for the generation of new carbon–carbon bonds. Carboranyllithium and carboranylcopper lithium reagents have been reported, but their synthetic applications are limited due to the harsh reaction conditions normally associated with these reagents. For example, the reaction of carboranylcopper lithium complex with *meso*-tetraphenylporphyrin provided only 7% yield of the desired carboranyl-substituted product, even after 12 days refluxing in diglyme.[31] Carboranyltrialkyltin reagents have been shown to react with aldehydes forming the corresponding addition products,[32] but these reagents have shown limited application in palladium-catalyzed cross-coupling reactions with aryl halides. We therefore decided to synthesize a carboranyl-substituted boronic acid and to investigate its usefulness in the preparation of carboranyl pyrroles and thiophenes. We have previously reported the preparation of carboranyl-substituted pyrroles,[33,34] but our synthetic routes involved 4–6 steps and consequently produced the target molecules in low overall yields. An alternative synthesis of these molecules would be via palladium-catalyzed cross-coupling reactions between readily accessible bromopyrroles and a carboranyl-substituted boronic acid.[35] Since the preparation of 1-boronic acid-*o*-carborane from *o*-carborane and $B(OCH_3)_3$ suffered from very low yields, we decided to synthesize boronic acid **3** bearing a methylphenyl spacer between the carborane and the boronic acid groups. The presence of this spacer did not only dramatically increase the yield of the target molecule but also minimized the steric hindrance effect during the coupling reaction with bromopyrroles (vide infra).

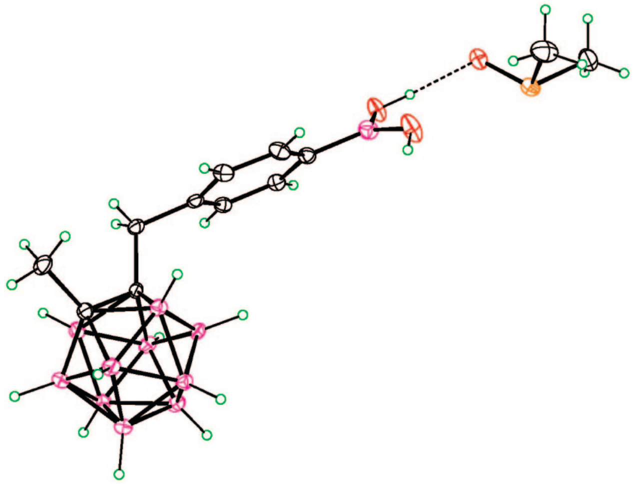


Figure 1. Molecular structure of boronic acid **3**.

Carboranylboronic acid **3** was synthesized using the route shown in Scheme 1, from commercially available **1** and 1-methyl-*o*-carborane, via the corresponding boronic ester **2** in 80% overall yield. The oxidation and hydrolysis of boronic ester **2** using sodium periodate in the presence of aqueous ammonium acetate[36] gave **3** in 89% overall yield. When the hydrolysis step was accomplished under acidic conditions, using 2 N HCl instead of aqueous ammonium acetate, lower yields of boronic acid **3** were obtained.[35] Under the acidic hydrolysis conditions the side product 4-(methylcarboranyl)methylphenyl iodide (**10**, R = I, vide infra) was obtained. Compounds **2** and **3** were characterized by NMR, MS, and, in the case of **3**, by X-ray crystallography. Figure 1 shows the structure of carboranyl boronic acid **3**. The $B(OH)_2$ moiety is twisted out of the phenyl plane by 33.5(2)° and has the expected conformation, in which one OH group is oriented *syn* and the other *anti*. The compound crystallizes as the 1:1 solvate with DMSO, and both OH groups form near-linear hydrogen bonds with DMSO oxygen (OO 2.739(2) and 2.823(2) Å), one of which is shown in Figure 1. Both **2** and **3** were used in the palladium(0)-catalyzed cross-coupling reactions with bromopyrroles.

3.2. Synthesis of Carboranylpyrroles. The synthesis of carbon–carbon-linked carboranyl-substituted organic molecules can be achieved via nucleophilic substitution reactions

---

(31) Frixa, C.; Mahon, M. F.; Thompson, A. S.; Threadgill, M. D. *Tetrahedron Lett.* **2002**, *43*, 1557.

(32) Nakamura, H.; Sadayori, N.; Sekido, M.; Yamamoto, Y. *J. Chem. Soc., Chem. Commun.* **1994**, 2581.

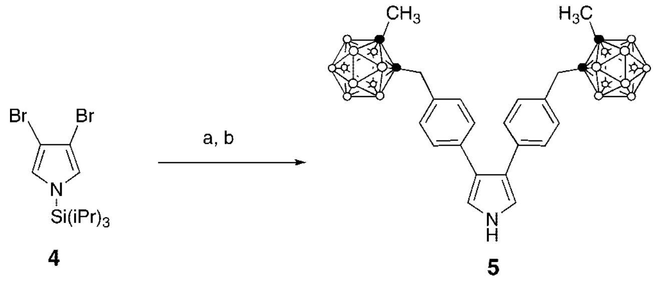
(33) Chayer, S.; Jaquinod, L.; Smith, K. M.; Vicente, M. G. H. *Tetrahedron Lett.* **2001**, *42*, 7759.

(34) Clark, J. C.; Fronczek, F. R.; Vicente, M. G. H. *Tetrahedron Lett.* **2005**, *46*, 2365.

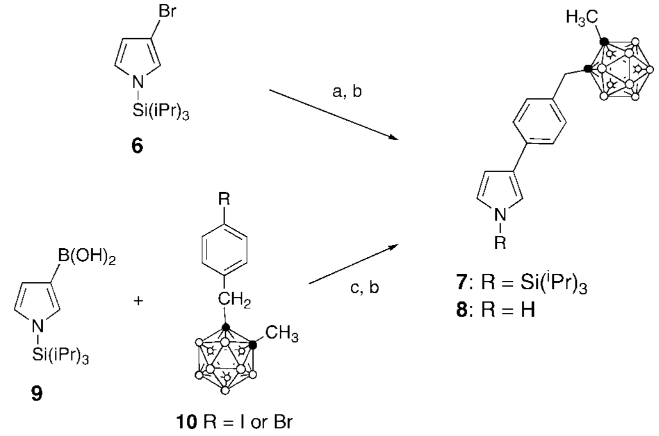
(35) Hao, E. H.; Fronczek, F. R.; Vicente, M. G. H. *Chem. Commun.* **2006**, 4900.

(36) Yu, S.; Saenz, J.; Srirangam, J. K. *J. Org. Chem.* **2002**, *67*, 1699.

Scheme 2. Reaction conditions: (a) compound 2 or 3, $Pd(PPh_3)_4$, $NaHCO_3$, toluene/methanol 5:1; (b) Bu_4NF, THF, 0 °C (32% overall)



Scheme 3. Reaction conditions: (a) compound 2 or 3, $Pd(PPh_3)_4$, $NaHCO_3$, toluene/methanol 5:1 (17%); (b) Bu_4NF, THF, 0 °C (95–100%); (c) Na_2CO_3, toluene/methanol 5:1 (89%)



using carboranyllithium and other metal complexes, in low to moderate yields.[37–41] Since these reaction conditions are not compatible with a variety of base-sensitive functional groups, another route for the synthesis of carbon–carbon-linked carboranyl molecules was developed, which involves the reaction of monosubstituted alkynes with activated boranes, $B_{10}H_{14}L_2$.[42–44] However, this strategy is also of limited applicability, usually affording low yields of the target molecules after long reaction sequences. We envisioned an alternative synthetic methodology for the preparation of carboranyl-substituted pyrroles and thiophenes using metal-catalyzed cross-couplings, as these reactions have found wide application in organic syntheses and would allow the readily preparation of a series of pyrrole and thiophene monomers for structure–property investigations of the corresponding polymers. Among these cross-coupling reactions, the Suzuki reaction[45] is particularly attractive because of its mild conditions and readily available bromopyrroles and pyrrole- and thiopheneboronic acids.

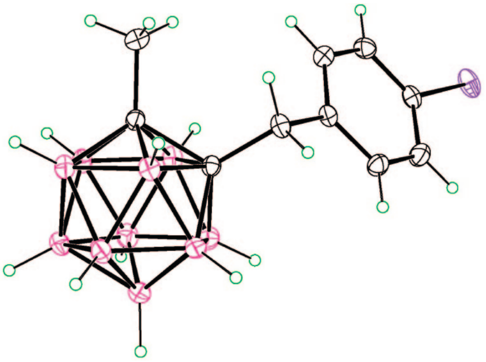


Figure 2. Molecular structure of iodide **10**.

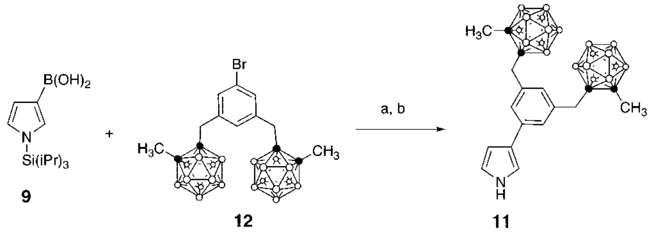
Commercially available dibromopyrrole **4** reacted with carboranylboronic ester **2** or boronic acid **3** in the presence of $Pd(PPh_3)_4$ to produce dicarboranylpyrrole **5**, after deprotection using tetrabutylammonium fluoride (Scheme 2). The yield for the coupling reaction depended on the solvent and base used, and the highest yield (32% overall) was obtained when $NaHCO_3$ and a 5:1 mixture of toluene and methanol were used. In anhydrous toluene using either K_2CO_3 or Na_2CO_3 as the base, the reaction was very slow and produced only ~3% of the target pyrrole **5**. This is probably due to the instability of the N-protected dibromopyrrole **4** under strongly basic conditions. We have previously reported the multistep synthesis of 3,4-dicarboranyl-substituted pyrroles from *o*-carborane in 21–54% overall yields.[13,14,33,34] In comparison with our previously reported routes, the new methodology outlined in Scheme 2 is faster and cheaper. Furthermore, we did not detect any side deboronation reactions of the *o*-carborane cages in the presence of tetrabutylammonium fluoride, since the cleavage of the triisopropylsilyl group took place at 0 °C in 15–20 min.

Using a similar strategy, monobromopyrrole **6** reacted with boronic ester **2** or with **3** to produce pyrrole **7** in only 17% yield due to the poor stability of pyrrole **6** under the basic reaction conditions (Scheme 3). In order to increase the yield of the target pyrrole **8**, an alternative approach was investigated, involving the coupling of commercially available pyrrole boronic acid **9** with a carboranyl–aryl halide **10**. Under these conditions the target pyrrole **8** was obtained in 89% yield.[35] The carboranyl–aryl halides **10** were prepared in high yield (75–79%) from commercially available bromomethyl bromo- or iodobenzene, as we have previously reported.[46] The structure of the new aryl iodide **10** (R = I) was confirmed by X-ray crystallography (Figure 2). The C–I distance is 2.0967(18) Å, and the iodobenzyl substituent is oriented essentially *anti* to a B of the carborane. Torsion angle B1–C2–C3–C4 is –172.79(15)°, and torsion angle

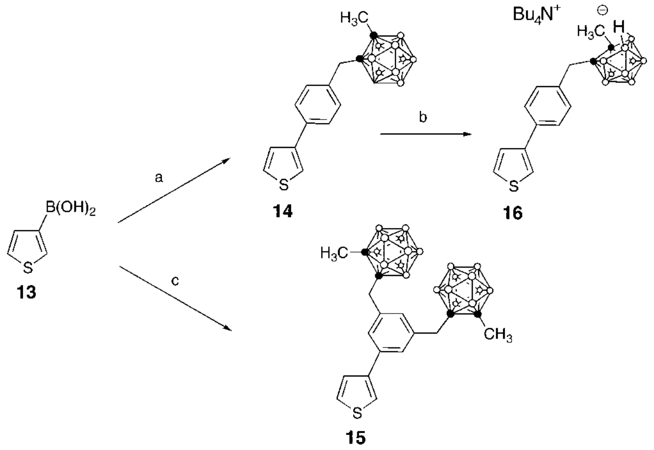
---

(37) Cheung, M-S.; Chan, H-S.; Xie, Z. *Dalton* **2005**, 2375.
(38) Zakharkin, L. I.; Kovredou, A. I.; Ol'shevskaya, V. A.; Shaugum-bekova, Z. S. *J. Organomet. Chem.* **1982**, *226*, 217.
(39) Zheng, Z.; Jiang, W.; Zinn, A. A.; Knobler, C. B.; Hawthorne, A. F. *Inorg. Chem.* **1995**, *34*, 2095.
(40) Marshall, W. J.; Young, R. J.; Grushin, V. V. *Organometallics* **2001**, *20*, 523.
(41) Kultyshev, R. G.; Liu, S.; Leung, H. T.; Liu, J.; Shore, S. G. *Inorg. Chem.* **2003**, *42*, 3199.
(42) Heying, T. L.; Ager, J. W.; Clark, S. L.; Mangold, D. J.; Goldstein, H. L.; Hillman, M.; Polak, R. J.; Szymanski, J. W. *Inorg. Chem.* **1963**, *2*, 1089.
(43) Bregadze, V. I. *Chem. Rev.* **1992**, *92*, 209.
(44) Valliant, J. F.; Guenther, K. J.; King, A. S.; Morel, P.; Schaffer, P.; Sogbein, O. O.; Stephenson, K. A. *Coord. Chem. Rev.* **2002**, *232*, 173.
(45) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457.
(46) Vicente, M. G. H.; Edwards, B. F.; Shetty, S. J.; Hou, Y.; Boggan, J. E. *Biorg. Med. Chem.* **2002**, *10*, 481.

Scheme 4. Reaction conditions: (a) $Pd(PPh_3)_4$, Na_2CO_3, toluene/methanol 5:1 (87%); (b) Bu_4NF, THF, 0 °C (96%)



Scheme 5. Reaction conditions: (a) 10 (R = Br), $Pd(PPh_3)_4$, Na_2CO_3, toluene/methanol 5:1 (94%); (b) Bu_4NF, THF, 60 °C (90%); (c) 12, $Pd(PPh_3)_4$, Na_2CO_3, toluene/methanol 5:1 (92%)



C1–C2–C3–C4 is –103.65(18)°.We have also previously reported the X-ray structure of pyrrole **7**.[35]

Using a similar synthetic strategy, the dicarboranylpyrrole **11** was prepared from the reaction of **9** with dicarboranylbromobenzene **12** in 89% overall yield (Scheme 4). Compound **12** was prepared from 3,5-dimethylbromobenzene in two steps, as we have previously reported.[47]

3.3. Synthesis of Carboranylthiophenes. The synthesis of 3-substituted carboranylthiophenes bearing a phenylmethyl spacer between the carborane and thiophene units is expected to reduce the oxidative voltage required for polymerization of these monomers and therefore the so-called "polythiophene paradox" effect.[27–29] The synthesis of functionalized thiophenes is in general easier than that of the analogue pyrroles because of the higher stability of thiophenes under a variety of reaction conditions and the shorter reaction sequences that do not require NH protection and deprotection steps. Since in the synthesis of carboranylpyrroles under Suzuki coupling conditions the use of pyrrole-3-boronic acid **9** and aryl halides **10** and **12** gave the highest yields of the target molecules, we applied a similar methodology to the preparation of carboranylthiophenes from thiophene-3-boronic acid (Scheme 5). Under these conditions carboranylthiophenes **14** and **15** were obtained in 94% and 92% yields, respectively. The structure of these new compounds was characterized by NMR, MS, and, in the case of **14**, X-ray crystallography. The molecular structure of thiophene **14** is shown in Figure 3, in which only one of the two disordered orientations of the thiophene ring is illustrated. The phenyl and thiophene rings are nearly coplanar, forming a dihedral angle of 4(1)°. The conformation of the phenyl substituent with respect to the carborane is similar to that seen in **10** (R = I), with relevant torsion angles B–C–C–C 177.0(1)° and C–C–C–C 108.3(1)°. The crystal data, data collection, and refinement parameters for compounds **3**, **10** (R = I), and **14** are given in Table 1. In order to investigate and compare the polymer properties resulting from electropolymerization of thiophenes bearing either a neutral carborane cage or an anionic nido cage, we prepared *nido*-carboranylthiophene **16** by deboronation of the *o*-carborane cage of thiophene **14** using tetrabutylammonium fluoride at 60 °C (Scheme 5).[48]

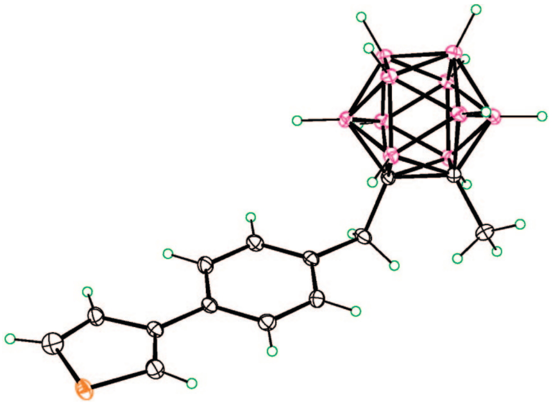


Figure 3. Molecular structure of carboranylthiophene **14**.

Table 2. Cyclic Voltammetry Data of Different Carboranyl-Substituted Pyrroles and Thiophenes at 10^{-2} M in CH_3CN or CH_2Cl_2 + 10^{-1} or 2×10^{-1} M Bu_4NPF_6 (Potential Scan Rate: 0.1 V s^{-1})

compound	E_{pa}^{mon}/V[a]	$E^{\circ\prime poly}$/V[b]	p-doping/n-doping levels
5	0.96[c]	0.26[c]	0.35–0.40
8	0.84[c]	−0.01[c]	0.20–0.25
11	0.92_5[c] 1.02[d]	[e] [f]	
14	1.53[d]	0.63/−1.90[d]	0.04/0.09
15	1.56[d]	0.58/−1.91[d]	0.13/0.02
16	0.56, 0.85 and 1.74[d]	[g]	

[a] Irreversible anodic peak potential corresponding to the monomer oxidation. [b] Formal potential corresponding to the reversible p (or n)-doping/undoping of the electrogenerated conducting polymer (average of anodic and cathodic peak potentials). [c] In CH_3CN. [d] In CH_2Cl_2. [e] The compound did not electropolymerize whatever the tested experimental conditions. [f] Formation of soluble electroactive oligomers. [g] Passivation of the electrode surface occurred.

3.4. Electrochemical Characterization of Carborane-Substituted Monomers and Corresponding Conducting Polymers. The cyclic voltammetry characterization of carborane-substituted pyrroles and thiophenes in CH_3CN or CH_2Cl_2 revealed one irreversible anodic peak in the range 0.84–0.96 and 1.53–1.74 V corresponding to the oxidation of the pyrrole and thiophene rings, respectively (Table 2). For thiophene **16**, two further irreversible anodic peaks

---

(47) Vicente, M. G. H.; Wickramasinghe, A.; Nurco, D. J.; Wang, H. J. H.; Nawrocky, M. M.; Makar, M. S.; Miura, M. *Biorg. Med. Chem.* **2003**, *11*, 3101.

(48) Fox, M. A.; MacBride, J. A. H.; Wade, K. *Polyhedron* **1997**, *16*, 2499.

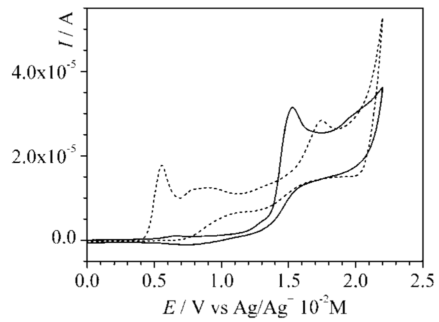


Figure 4. Cyclic voltammograms at 0.1 V s^{-1} in $CH_2Cl_2 + 2 \times 10^{-1}$ M Bu_4NPF_6 of **14** (solid line) and **16** (dashed line) at 10^{-2} M.

assigned to the oxidation of the anionic carborane cage were also observed at less positive potentials (Figure 4).

Among the carboranylpyrroles, the oxidation of **5** and **8** led to the formation of conducting polymer deposits on the electrode surface. Such films could be electrogenerated either potentiodynamically or potentiostatically with no significant effect of the electropolymerization method on their respective electrochemical responses. As an example, typical cyclic voltammograms corresponding to the potentiodynamical electropolymerization of **8** are shown in Figure 5A. The analysis of poly(**8**) in a monomer-free electrolytic solution showed a broad reversible redox system at ca. 0 V corresponding to the p-doping/undoping of the polypyrrole backbone (Figure 5B). Compared with **8**, pyrrole **5** and its corresponding electrogenerated polymer were oxidized at more positive potentials as a result of the presence of two sterically hindered carborane cages, rather than one, on the pyrrole ring (Table 2). These results are in agreement with our previous investigations of the electrochemical behavior of monocarboranylpyrroles, bearing one or two methylene spacers between the carborane and pyrrole units.[12,13] However, in comparison with poly(3-phenylpyrrole) and poly(3,4-diphenylpyrrole), poly(**5**) and poly(**8**) were found to be more easily oxidizable which indicates a more conjugated structure, as was also supported by the UV–vis spectroscopy data (vide infra). From the integration of the cyclic voltammetry curve, the p-doping level δ_p of poly(**5**) and poly(**8**) was estimated respectively at 0.35–0.40 and 0.20–0.25 positive charge per monomer unit, using eq 1:

$$\delta_p = \frac{2Q_a}{Q_s - Q_a} \qquad (1)$$

where Q_a is the anodic charge under the polymer voltammetric response and Q_s is the electropolymerization charge.

In contrast to the readily electropolymerization of **5** and **8**, pyrrole **11** did not yield a conducting polymer deposit under a variety of experimental conditions, for example using different monomer concentrations, oxidation potentials, solvents and methods, possibly due to the high steric hindrance of its 3-dicarboranylmethylphenyl substituent. However, the electropolymerization of its analogous dicarboranylarylthiophene **15** was feasible at high potential values (1.56 V). Indeed, its electropolymerization potential was very close to that observed for **14**. The electrochemical response of poly(**14**) and poly(**15**) films showed two reversible systems at ca. 0.60 and −1.90 V corresponding to p- and n-doping processes respectively (Figure 6). Surprisingly and unlike the polypyrrole derivatives, the position of these two systems was not significantly dependent on the number of carborane cages on the polythiophene backbone. The electrochemically determined δ_p and n-doping levels δ_n for poly(**14**) and poly(**15**) were significantly different. Values of $\delta_p = 0.04$ and $\delta_n = 0.09$ were calculated for poly(**14**) against 0.13 and 0.02 for poly(**15**). Globally, the p- and n-doping levels of these polymers are smaller than those reported for other poly(3-arylthiophene)s,[49,50] which demonstrates the prominent role of the carborane cages on the ion transport in these films. As observed for poly(**5**), the number of positive charges along the polythiophene chain was enhanced with increasing number of grafted carborane groups. These results cannot be explained solely on the basis of electronic and steric considerations, as the inverse situation should be encountered; rather, these values could be due to morphological differences between the polymers. Perhaps the presence of two carborane cages per pyrrole or thiophene ring could favor the formation of more opened polymer structures and thus facilitate the ion transport through the film.

In **16**, the oxidation of the anionic *nido*-carborane cage before that of the aromatic ring inhibited the electropolymerization reaction. Instead, passivation of the electrode surface occurred as revealed by the progressive decrease of the oxidation current with the number of scans. No visible film was detected on the electrode surface. These results are consistent with those reported for 3-substituted pyrroles bearing anionic carborane groups.[13]

The effect of highly positive potentials on the electroactivity of the electrogenerated polymers was also examined. Polypyrroles and polythiophenes are known to be highly sensitive to overoxidation[51–53] where, at high potentials, the electroactivity and conductivity of the polymer films are degraded as a result of nucleophilic attack on the five-membered rings. In previous reports, we showed that the introduction of carborane cages on polypyrrole through a short alkyl spacer increased its resistance to electrochemical overoxidation.[12,13] As shown in Figure 7, the use of a benzylic spacer between the pyrrole and carborane units resulted in complete destruction of the electroactivity of poly(**5**) and poly(**8**) after two scans until 2.0 V. In contrast, the overoxidation resistance of poly(**14**) and poly(**15**) were considerably higher, and an electroactivity loss of only 5–10% was observed after five scans. On the other hand, a similar treatment rendered the parent polythiophene film totally electroinactive after three scans. The above differences observed for the polypyrrole and polythiophene derivatives are not straightforward to explain. It is well-known that unsubstituted polypyrrole is less stable to increasing oxidizing potentials than polythiophene with an irreversible overoxidation peak occurring at less positive potentials.[53] Moreover,

---

(49) Guerrero, D. J.; Ren, X.; Ferraris, J. P. *Chem. Mater.* **1994**, *6*, 1437.
(50) Sarker, H.; Gofer, Y.; Killian, J. G.; Poehler, T. O.; Searson, P. C. *Synth. Met.* **1997**, *88*, 179.
(51) Beck, F.; Braun, P.; Oberst, M. *Ber. Bunsenges. Phys. Chem.* **1987**, *91*, 967.
(52) Barsch, U.; Beck, F. *Electrochim. Acta* **1996**, *41*, 1761.
(53) Schlenoff, J. B.; Xu, H. *J. Electrochem. Soc.* **1992**, *139*, 2397.

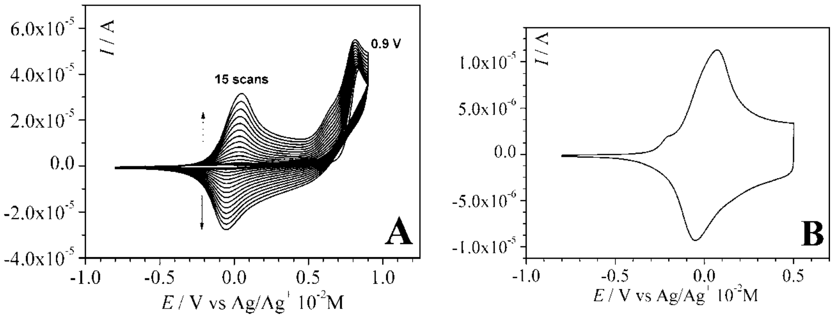


Figure 5. (A) Successive cyclic voltammograms of **8** at 10^{-2} M in $CH_3CN + 10^{-1}$ M Bu_4NPF_6 (0.1 V s^{-1}). (B) Electrochemical response of the electroformed polymer in $CH_3CN + 10^{-1}$ M Bu_4NPF_6 at 0.1 V s^{-1} (electropolymerization charge: 64 mC cm^{-2}).

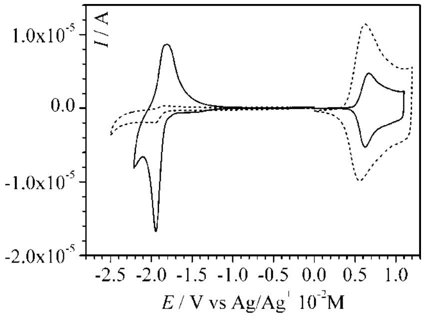


Figure 6. Cyclic voltammograms at 0.1 V s^{-1} of (solid line) poly(**14**) and (dashed line) poly(**15**) in $CH_2Cl_2 + 2 \times 10^{-1}$ M Bu_4NPF_6. The electropolymerization charge is 127 mC cm^{-2}.

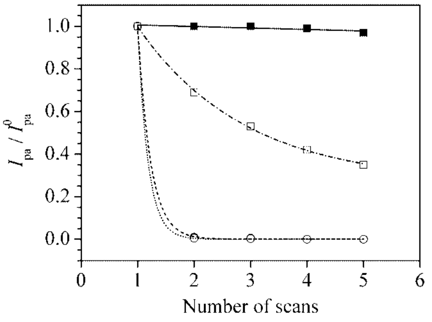


Figure 7. Resistance to highly positive potentials of (●) poly(**5**), (○) poly(**8**), (□) poly(**14**), and (■) poly(**15**) cycled until 2 V vs Ag/Ag^+ 10^{-2} M at 0.1 V s^{-1}. I_{pa} and I^0_{pa} correspond to the polymer anodic peak current intensities observed in the *n*th and first scans, respectively. The electropolymerization charge is 127 mC cm^{-2}.

it must be noted that the first step in the overoxidation process is usually a nucleophilic attack of the oxidized aromatic rings by hydroxide ions present in the electrolytic solution.[51–53] Since poly(**5**) and poly(**8**) are much more positively doped than poly(**14**) and poly(**15**), it is likely that this reaction is favored for poly(**5**) and poly(**8**).

3.5. UV–vis Spectroscopy Analysis of Polymers. To gain further insight into the electronic properties of carborane-substituted polypyrroles and polythiophenes, a UV–vis spectroscopy analysis was performed for the electrochemically reduced and p-doped forms of the polymers. In the reduced state we observed strong absorption bands due to the interband $\pi \rightarrow \pi^*$ transition of the chain of conjugated pyrrole rings at 346 nm (3.6 eV) and 390 nm (3.2 eV) for poly(**5**) and poly(**8**), respectively, as shown in Figure 8. It must be noted that the monomers do not show any absorption band beyond ca. 300 nm. Our values indicate that poly(**5**) is less conjugated than poly(**8**), and the large band gap can be explained by a more pronounced twisting from planarity of the pyrrole rings in poly(**5**) as a result of the 3,4-disubstitution. Within the gap region, there is an additional band at ca. 850 nm for both polymers due to the difficulty in completely reducing the polypyrrole electrochemically to its totally neutral form, in agreement with previous reports on other perchlorate-doped polypyrrole films.[54–56] Compared with poly(3-phenylpyrrole)[57] and poly(3,4-diphenylpyrrole),[58] the absorbance peaks of the $\pi \rightarrow \pi^*$ transition band in poly(**5**) and poly(**8**) are shifted to longer wavelengths, indicating a more conjugated structure. For the oxidatively doped polymers, the spectra are characterized by two absorption bands at 476 nm (2.6 eV) and above 1100 nm (<1.1 eV) for poly(**5**) and 495 nm (2.5 eV) and 875 nm (1.4 eV) for poly(**8**). These results are consistent with the formation of bipolaronic states in the as-grown poly(**5**) and the coexistence of polaronic and bipolaronic states in the as-grown poly(**8**).[54–56] Furthermore, such results are in perfect agreement with the higher doping level calculated for poly(**5**).

For the polythiophene derivatives, the absorption maximum for the interband $\pi \rightarrow \pi^*$ transition is observed at 471 nm (2.6 eV) and 492 nm (2.5 eV) for electrochemically reduced poly(**14**) and poly(**15**), respectively (Figure 8C, D). The onset of this band was used to determine the optical band gap of these polymers. Values of 2.1 and 1.95 eV were calculated for poly(**14**) and poly(**15**), which are consistent with the electrochemical band gaps determined from the potential differences between the onset of the p- and n-doping redox waves, namely 2.15 and 2.00 eV for poly(**14**) and poly(**15**), respectively (Figure 6). In spite of the presence of two carborane units, poly(**15**) is more conjugated than poly(**14**), and its band gap is similar to that reported for poly(3-phenylthiophene).[59] These results and those obtained for the polypyrrole derivatives allow us to conclude that the substitution of the phenyl ring by methylcarboranyl group(s) does not change or increase the mean conjugation length of the resulting polymers.

---

(54) Brédas, J. L.; Street, G. B. *Acc. Chem. Res.* **1985**, *18*, 309.
(55) Yakushi, K.; Lauchlan, L. J.; Street, G. B.; Brédas, J. L. *J. Chem. Phys.* **1984**, *81*, 4133.
(56) Brédas, J. L.; Scott, J. C.; Yakushi, K.; Street, G. B. *Phys. Rev. B* **1984**, *30*, 1023.
(57) Masuda, H.; Kaeriyama, K. *Synth. Met.* **1990**, *38*, 371.
(58) Feldheim, D. L.; Hendrickson, S. M.; Krejcik, M.; Elliott, C. M. *Chem. Mater.* **1995**, *7*, 1124.
(59) Naudin, E.; El Medhi, N.; Soucy, C.; Breau, L.; Bélanger, D. *Chem. Mater.* **2001**, *13*, 634.

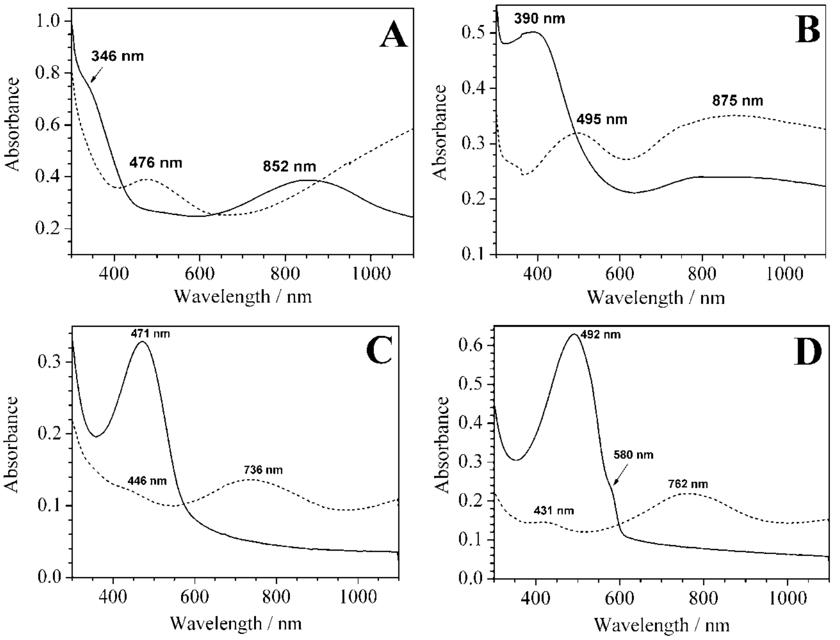


Figure 8. Solid-state UV–vis spectra of (A) poly(**5**), (B) poly(**8**), (C) poly(**14**), and (D) poly(**15**): (dashed) freshly as-grown PF_6^--doped films and (solid) undoped electrochemically at –1.5 V until almost zero current.

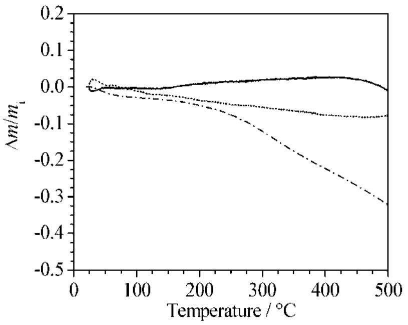


Figure 9. TGA curves of (solid line) poly(**8**), (dashed line) poly(**5**), and (dash-dotted line) polypyrrole in the neutral state under N_2. Weight of the polymers: 2.5–3 mg.

The as-grown p-doped poly(**14**) and poly(**15**) films were characterized by one main broad band with a maximum located at 736 and 762 nm, respectively, along with a weak shoulder at 446 and 431 nm, respectively. Thus, similarly to the neutral forms, the main band of the oxidized poly(**15**) was red-shifted by the same extent with respect to that of poly(**14**). The position of this doping-induced band and the lowly doped character of the as-grown polymers indicate the formation of polaronic charge states along the polymer chain.

3.6. Thermal Stability of the Polymers. The covalent modification of conducting polymers with carborane cages was also found to dramatically increase the thermal stability of the polymers. As an example, the thermogravimetric analysis (TGA) of undoped poly(**5**) and poly(**8**) is shown in Figure 9. The TGA was performed under N_2 up to 500 °C. Compared with TGA of unsubstituted polypyrrole, there is only a slight loss in the mass of poly(**5**) (ca. 8%) and poly(**8**) (ca. 1%) up to 500 °C. For the parent polymer, there was a continuous loss in mass, reaching ~40% at 500 °C. These results are in agreement with those previously reported for a carboranylpyrrole bearing a two methylene spacer between the pyrrole and carborane units.[13] Unfortunately, similar experiments with electrogenerated poly(**14**) and poly(**15**) could not been achieved. Indeed, the decrease in the electropolymerization yield with increasing the film thickness and the weak adherence of these electrogenerated films to the electrode surface did not enable us to retrieve a sufficient amount of polymer for further TGA measurements. Attempts to produce more polymer through chemical polymerization are currently in progress. However, it is likely that the thermal behavior of the polythiophene derivatives is similar to that observed for poly(**5**) and poly(**8**). We have recently reported that poly[di(2-thiophenyl)-*o*-carborane] also shows very high thermal stability.[60]

4. Conclusions

A series of 3-mono- and 3,4-disubstituted pyrroles and thiophenes bearing bulky carborane groups linked via a methylphenyl spacer have been synthesized via Pd(0)-catalyzed cross-coupling reactions. This methodology allows the expeditious preparation of the target compounds in high yields. Among these, derivatives **5**, **8**, **14**, and **15** yielded the corresponding functionalized conducting polymer films by anodic oxidation in acetonitrile or dichloromethane medium. The pyrrole-based polymers poly(**5**) and poly(**8**) were oxidized at less positive potentials compared with poly(3-phenylpyrrole) and poly(3,4-diphenylpyrrole), which is consistent with a more conjugated structure, as supported by UV–vis spectroscopy measurements. The thiophene-based polymers poly(**14**) and poly(**15**) showed reversible p- and n-doping redox waves in the same potential range than those observed for poly(3-phenylthiophene). Furthermore, the mean conjugation length of poly(**15**) bearing two carborane cages per monomer unit was unexpectedly similar to that of so-called

---

(60) Hao, E.; Fabre, B.; Fronczek, F. R.; Vicente, M. G. H. *Chem. Commun.* **2007**, 4387.

highly conjugated poly(3-phenylthiophene). The electroactivity of poly(**5**) and poly(**8**) was totally degraded when highly oxidizing potentials were applied. In contrast, this electrochemical treatment had a limited effect on the electroactivity of poly(**14**) and poly(**15**) which might be due to the presence of the carborane cages linked to the polymer matrix. Moreover, the introduction of these functional moieties was found to dramatically increase the thermal stability of the polymers.

Acknowledgment. We thank the National Institutes of Health, Grant CA098902, for financial support of this research. Y. Le Gal (Unité Mixte de Recherche n°6226 CNRS/Université de Rennes 1, France) is also fully acknowledged for TGA measurements.

Supporting Information Available: X-ray data in CIF format for **3**, **10**, and **14**. This material is available free of charge via the Internet at http://pubs.acs.org.

CM701935N